# VOC Surveillance using EPA's Trace Atmospheric Gas Analyzer (TAGA) and ASPECT Aerial Platform FTIR

In a heavily industrialized area in Southeast Texas, EPA atmospheric scientists recently conducted an inter-comparison study of the EPA mobile Trace Atmospheric Gas Analyzer (TAGA) and the ASPECT Aerial Platform FTIR. The TAGA is a mobile air sampling device that is capable of detecting a wide-range of volatile organic compounds in ambient air in the Part Per Trillion range. The ASPECT aerial platform FTIR is an aircraft mounted Fourier Transform Infrared detector that includes a 16 band line scanner, thermal imaging camera and digital camera. The ASPECT generally



detects most VOCs in the low part per million range although significantly lower detection levels are possible for select chemical species. For this study, fenceline monitoring with the TAGA was conducted while aerial platform ASPECT recordings were conducted. Results of this investigation are presented below.

The purpose of the project is to determine the concentration and distribution of the pollutants of concern in the Jefferson County (urban) area. The Jefferson County area, as designated by the U.S.EPA, consists of the Assessment Areas of Port Neches, Beaumont, and Port Arthur. To the north and east of these urban areas is the Neches River and beyond that is primarily inaccessible wet land. The monitoring of Urban Air Toxics, therefore, concentrated on the urban/industrial areas of Port Neches, Beaumont, and Port Arthur.

There are currently 188 hazardous air pollutants (HAPs), or air toxics, regulated under the Clean Air Act as a result of the Clean Air Act Amendments of 1990. These pollutants have been associated with a wide variety of adverse health effects.

The U.S.EPA has identified 33 of the 188 HAPs, as posing the greatest threat to public health in urban areas. These HAPs include 18 volatile organic compounds (VOCs), 9 metals/metal compounds, and 6 other HAPs. To respond to this public health threat, the U.S.EPA has established a national effort to reduce air toxics from mobile and stationary sources. On July 19, 1999, the U.S.EPA published its Urban Air Toxics Strategy (Strategy) in the *Federal Register*.

A critical element of this Strategy is to move to a more risk-based program for reducing HAPs, particularly in urban areas. Urban areas are an important focus for research needs, since these areas are typically heavily industrialized, densely populated, and tend to be economically disadvantaged. Additionally, multiple sources of a combination of HAPs create a combined toxic effect that is not usually accounted for in typical assessments.

In support of the Strategy and to obtain sufficient ambient air monitoring data, the U.S.EPA, Office of Air Quality Planning and Standards developed a draft Air Toxics Monitoring Concept Paper. This Concept Paper recognizes the need for a national ambient air toxics monitoring network, stresses the need to build upon existing monitoring programs, and cites the need to take advantage of mobile and stationary monitoring resources.

The U.S. EPA has designated a number of assessment areas to be monitored for Urban Air Toxics. U.S. EPA Region VI has included southeastern Texas, Jefferson County, which is a heavily industrialized corridor, and, based upon data reported to the 1996 National-scale Air Toxics Assessment program, had the worst ambient air quality of all counties in the five state region.

According to a report published by a coalition of the National Environmental Trust, Physicians for Social Responsibility and Learning Disabilities Association of America; Louisiana and Texas lead the nation in air emissions of developmental and neurological toxins, with the most common sources being manufacturing, petroleum refining, and



paper manufacturing. Jefferson County is densely populated with these types of industrial facilities. Additionally, Jefferson County has several minority or low-income communities, which are typically at greater risk of exposure to toxic substances.

More information is needed in this corridor to identify disproportionally impacted urban areas and to quantify risks based on commutative air toxic concentrations. Identifying sources of contamination that contribute to the cumulative air pollution will also assist in more effective and targeted enforcement by the U.S. EPA. Areas identified in Jefferson County for further assessment include the Beaumont Assessment Area, the Port Neches Assessment Area, and the Port Arthur Assessment Area.

The U.S. EPA Environmental Response Team Center (ERTC), has a variety of state-of-technology instrumentation to

monitor for air toxics. This instrumentation includes two ECA Trace Atmospheric Gas Analyzer IIe (TAGA) Mobile Laboratories. The TAGA Mobile Laboratories are capable of monitoring, in real-time, trace levels of many organic and inorganic compounds in ambient air. The U.S.EPA Region VI has thereby requested that the ERTC assist in the Urban Air Toxics Monitoring program by using the TAGA Mobile Laboratory to monitor for selected HAPs in the Jefferson County area. The TAGA IIe, (tandem quadrupole spectrometer) mounted in the TAGA Mobile Laboratory, is a rugged, reliable, and yet sensitive monitoring instrument capable of detecting low concentrations (parts per billion by volume [ppbv]) in various locations including, rural, industrial, residential and urban areas.

### Mass Spectrometer/Mass Spectrometer General Theory

The ECA TAGA IIe is based upon the Perkin-Elmer Sciex API 365 mass spectrometer/mass spectrometer (MS/MS) and is a direct air sampling instrument capable of detecting, in real time, trace levels of many volatile compounds in ambient air. The technique of triple quadrupole MS/MS is used to differentiate and quantitate compounds.

The initial step in the MS/MS process involves simultaneous chemical ionization of the compounds present in a sample of ambient air. The ionization can produce both positive and negative ions by donating or removing one or more electrons. Chemical ionization is a "soft" ionization technique, which allows ions to be formed with little or no

structural fragmentation. These ions are called parent ions. Parent ions with different mass-to-charge (m/z) ratios are separated by the first quadrupole (the first MS of the MS/MS system). The quadrupole scans selected m/z ratios allowing only the parent ions with these ratios to pass through the quadrupole. Parent ions with m/z ratios different than those selected are discriminated electronically and fail to pass through the first quadrupole.

The parent ions selected in the first quadrupole are accelerated through a collision cell containing uncharged nitrogen molecules in the second quadrupole. A portion of the parent ions entering the second quadrupole fragment as they collide with the nitrogen molecules. These fragment ions are called daughter ions. The process of fragmenting parent ions by impacting them with nitrogen molecules in the second quadrupole is called collision induced dissociation (CID). The daughter ions are separated according to their m/z ratios by the third quadrupole (the second MS



of the MS/MS system). The quadrupole scans selected m/z ratios, allowing only the daughter ions with the selected ratios to pass through the quadrupole. Daughter ions with the selected m/z ratios are then counted by an electron multiplier. The resulting signals are measured in ion counts per second (icps) for each parent/daughter ion pair selected. The intensity of the icps for each parent/daughter ion pair is directly proportional to the ambient air concentration of the compound that produced the ion pair. All of the ions discussed in this report have a single charge. The m/z ratios of all of the ions discussed are equal to the ion masses in atomic mass units (amu). Therefore, the terms parent and daughter masses are synonymous with parent and daughter ion m/z ratios.

#### **Pollutants of Concern**

A review of the HAP emissions inventory for the Jefferson County area and the 33 Urban Air Toxics, revealed the following pollutants to be of concern:

Benzene 1,3-Butadiene Chloroform

Carbon Tetrachloride 1,2-Dibromoethane 1,2-Dichloropropane 1,3-Dichloropropene 1,2-Dichloroethane 1,1,2,2-Tetrachloroethane Tetrachloroethene 1,1,2-Dichloropropane 1,2-Dichloroethane Tetrachloroethene

Vinyl Chloride

#### **Data Quality Objectives**

Monitoring for air toxics was performed in the field primarily with the U.S.EPA/ERTC's ECA TAGA IIe instrument although this project also included a photoionization detector, offsite TO-15 analysis, and the ASPECT FTIR. TAGA monitoring consisted of both mobile and stationary TAGA Mobile Laboratory analysis. The TAGA performed real-time monitoring throughout the Port Neches, Beaumont, and Port Arthur Assessment Areas for the pollutants of concern using a selected positive ion technique.

The TAGA instrument identifies pollutants based upon specific parent and daughter ions. The parent and daughter ions that have been determined appropriate for the thirteen pollutants of concern. Due to the need to identify the pollutants, irrespective of potential interferences, more than one set of parent/daughter ions were selected and applied to this effort. The TAGA instrument and associated software accumulated the ion counts per seconds for each parent/daughter ion pair selected. This raw data was retained by the on-board data collection system. In addition, handwritten operators' notes citing location and/or events were recorded.

To identify the geographic location of the TAGA Mobile Laboratory while ambient air quality monitoring data was being gathered, an on-board Global Positioning Satellite (GPS) system was employed. Positions conveyed by this system are expected to be accurate to within 2 meters, with real-time or post processing correction.

To assist in the TAGA ambient air monitoring effort, additional ambient air monitoring was performed using a photo-ionization detector (PID) MultiRAE with data logging capabilities. This PID obtained ambient air from the same sampling port as the TAGA IIe instrument. When the PID indicates ambient concentrations above 1 ppmv (part per million by volume), a sample of ambient air was collected in a Summa canister using grab sampling techniques. Similarly, when the TAGA detected ambient concentrations above 50 ppbv (parts per billion by volume), a sample of ambient air was collected in a Summa canister. All such samples were collected from the same sampling port as the TAGA instrument. The U.S.EPA Region VI Houston Laboratory analyzed samples collected in the Summa canisters for VOCs by U.S.EPA Method TO-15.

Meteorological data was downloaded from several met stations maintained by the Texas Commission on Environmental Quality (TCEQ). The TCEQ has a state-wide network of meteorological stations with data available real time in 5-minute averages. TCEO met data was obtained from the following four meteorological stations:

Name	Location	Data Available	
Port Neches	29 Deg 59' 27" N, 93 Deg 57' 12" W	Wind Speed (WS), Wind Direction (WD), Temp, Deviation of WD (DWD)	
Carol State Park	30 Deg 4' 1" N, 94 Deg 4' 38" W	WS, WD, DWD, Temp,	
Beaumont	30 Deg 2' 22" N, 94 Deg 4' 29" W	WS, WD, DWD, Temp, Solar Radiation	
Port Arthur	29 Deg 53' 39" N, 93 Deg 59' 15" W	WS, WD, DWD, Temp, Solar Radiation	

The ASPECT aerial platform FTIR is a mobile FTIR system housed in an Aerocommander airplane. The instrumentation generally detects various volatile organic chemicals (VOCs) in the low part per million range although significantly lower detection levels are possible for select chemical species. The ASPECT aerial platform FTIR is an aircraft mounted Fourier Transform Infrared detector that includes a 16 band line scanner, thermal imaging camera and digital camera.

#### DATA RESULTS

#### **ASPECT Data Results**

The ASPECT collected evening and night time line scanner and digital imagery on two successive nights in southeast Texas. Only one image detected absorption of infrared light in any of the wavelengths

investigated for this study. Appendix A shows a potentially leaking seal on an above ground storage tank that likely contains benzene. Detection limits for the ASPECT were likely in the 1 to 100 part per million (volume) range although additional dispersion modeling or ground level fugitive leak sampling would help provide a more accurate approximation of ground level VOC concentrations. One characteristic of airborne platform remote sensing is that all contaminants that absorb a portion of the light are collapsed into a horizontal plane when projected onto a 2- dimensional plane such as an aerial photograph. Three dimensional concentration data could only be detected using this method if additional dispersion modeling was performed or improvement in light detection and ranging (LIDAR) methodologies facilitate 3 dimensional depth and concentration data. This method of remote sensing is of significant value in large oil or chemical spills or releases of substances that are at significantly different temperatures or absorptions of infrared light. The current state of the science



does not appear to be adequate to detect a range of potentially toxic or carcinogenic substances in ambient air although for some select substances the methodology may bear investigation as a substantial investigative tool.

### Trace Atmospheric Gas Analyzer Results

Trace Atmospheric Gas Analyzer (TAGA) sampling was collected on four consecutive evenings from generally 8:00 pm until approximately 4:00 am the following morning. Results of these efforts are presented in Appendix B. Results indicate that VOC concentrations in the area were relatively low during the study period although several areas indicate future focus is warranted. Short term releases of benzene and several other chemicals of concern were detected above quantification levels although concentrations appeared to dissipate within the study area and were substantially below Occupational Safety and Health Administration(OSHA) Permissible Exposure Levels (PELs) for worker protection. Several chemicals exhibited short term concentrations above the Texas Health Effect Screening Levels although daily monthly and annual concentrations would likely be consistent with these values. Please note that on several occasions instrument error occurred just as the run was being terminated that resulted in a single spike in apparent concentration for various chemicals of concern. This anomaly has been attributed to an apparent voltage spike as the instrument is being shut down. ERT scientists will investigate this technical difficulty to attempt to eliminate this instrument error in future field work.

#### **CONCLUSIONS**

Sampling results indicate that VOC concentrations in the area were relatively low during the study period. Both instruments were field rugged and portable and required significant operator technical ability to

accomplish the mission.

Aerial platform spectroscopy appears to be of significant value in large oil or chemical spills or releases of substances that are at significantly different temperatures or absorptions of infrared light. The current state of the science does not appear to be adequate to detect a range of potentially toxic or carcinogenic substances in ambient air although for some select substances the methodology may bear investigation as a substantial investigative tool.

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#### REFERENCES

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U.S. Environmental Protection Agency. 1999. EPA Requirements for Quality Assurance Project Plans: EPA QA/R-5, Interim Final. November 1999.

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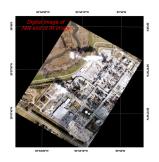
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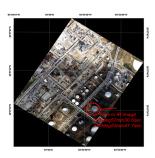
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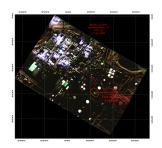
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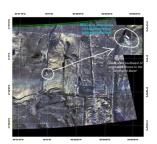
# **APPENDIX A**

Photos show a potentially leaking seal on an above ground storage tank that likely contains benzene.





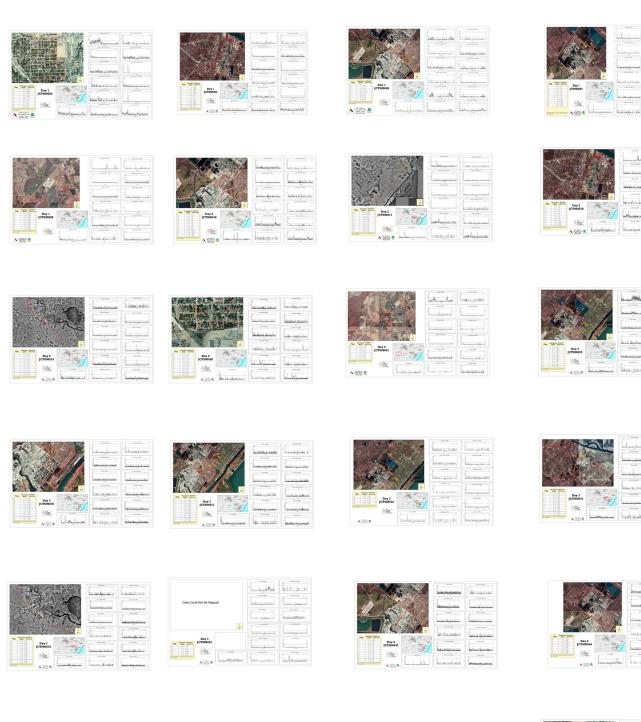




# **APPENDIX B**

Results indicate that VOC concentrations were relatively low during the study period although several areas indicate future focus is warranted.

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